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Sorption of inorganic radiocarbon on iron oxides

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Abstract

The sorption of inorganic radiocarbon on goethite, hematite and magnetite was studied as a function of carbon concentration, pH and ionic strength. It was discovered that the sorption of radiocarbon on magnetite was negligible in all studied conditions. The distribution coefficients of radiocarbon on hematite and goethite decreased with increasing pH whereas the ionic strength had only a slight decreasing effect on radiocarbon sorption. The sorption on goethite and hematite was modelled with PhreeqC using a generalized double-layer surface complexation model.

Keywords

radiocarbon, sorption, nuclear waste, goethite, hematite, magnetite

Introduction

Radiocarbon, ^{14}C, is assumed to be the most critical radionuclide, in addition to ^{36}Cl and ^{129}I, with respect to prospective radiation doses to human resulting from the final disposal of spent nuclear fuel in the future [1]. ^{14}C is a pure beta emitter and the maximum energy of its beta particles is 156 keV with a half-life of 5730 years. In Finland, the spent nuclear fuel will be disposed of at the depth of about 400 meters in a bedrock repository. The disposal will not include fuel reprocessing and thus the material to be disposed of consists of the actual fuel material, i.e. irradiated uranium dioxide, as well as the Zircaloy cladding and the metallic parts of the fuel assembly. In these, ^{14}C is produced when

neutrons activate the nitrogen in the materials with the reaction $^{14}N(n,p)^{14}C$. It can be found in the fuel material, Zircaloy cladding and steel structures in approximately equal portions [2]. Furthermore, one tenth of radiocarbon is assumed to occur in the easily soluble instant release fraction in fuel rod gaps and grain boundaries of the spent nuclear fuel [3]. The chemical forms of ^{14}C in the fuel and metallic structures are still unclear but it is assumed to occur as sparingly soluble carbide and elemental carbon [4-6]. Radiolysis caused by the radiation from the nuclear fuel may, however, oxidize these sparingly soluble species into more soluble species, for instance, carbon dioxide.

Very reducing conditions are prevailing at the Olkiluoto final disposal depth of approximately 400 meters, which implies that the plausible oxidation state of carbon is –IV and that the chemical form of carbon is methane and partly higher hydrocarbons. The study of Pitkänen and Partamies [7] has confirmed this when they determined the chemical forms of dissolved carbon in the groundwater of Olkiluoto. While dissolved carbon in the surface soil and in the upper parts of the bedrock is mainly as carbonate, its concentration being up to 80 mg/l, the methane concentrations in these layers are very low at concentrations less than 1 mL/L. At the disposal depth the situation is vice versa as the carbonate concentration is at a few mg/L and that of methane a few hundred mL/L. It is thus reasonable to assume that if any carbon is released from the fuel as carbon dioxide it will be reduced to methane. Methane dissolved into water will not be retained on the mineral surfaces but it can be transported in water conducting fractures closer to the biosphere and, furthermore, be oxidized to carbonate at layers closer to ground surface. In reality, very little is known about the behavior of ^{14}C in the bedrock and soil. As a result, in the safety analysis it is conservatively presumed that ^{14}C is not retained at all in the bedrock but is transported at the velocity of the groundwater flow.

Carbon occurs in the solid state in the bedrock either as calcite ($CaCO_3$) or graphite, which both are common fracture minerals in the Olkiluoto bedrock together with pyrite and clay minerals, such as kaolinite and illite [8]. In addition, carbon may occur in the bedrock as siderite ($FeCO_3$). ^{14}C can be retained as carbonate on calcite and siderite through isotope exchange [9-10]. There is constant dissolution and precipitation at equal rates of calcite in solubility equilibrium with groundwater and, thus, also ^{14}C as carbonate

($^{14}CO_3^{2-}$) in equilibrium with calcite water system will precipitate as carbonate in the system.

In addition to calcite and siderite, ^{14}C as carbonate can be retained on the surfaces of iron oxide minerals, the surfaces of which are at least partly positive due to the protonation of the hydroxyl groups [11]. The formation of a monodentate inner-sphere carbonate surface complex has been suggested as a possible adsorption reaction of carbonate on goethite based on ATR-FTIR studies [12-13] whereas bidentate complexation on hematite has been claimed by Brechbühl et al. [14]. Protonation and the positive charge of the minerals surfaces is highly pH dependent: the lower the pH, the higher the positive charge. The surface charge of iron oxides in groundwater in the typical pH range of 8-9 is mostly neutral and thus sorption is presumably low.

The sorption of ^{14}C as carbonate in goethite, hematite and magnetite was studied here as a function of carbon concentration. In addition, the effect of competing ions and pH was investigated and the results were modelled with PhreeqC. The isoelectric points (IEP) and the specific surface areas of the studied minerals was determined to support the modelling of the results. The three iron oxides used in this study represent iron oxides at various environmental redox conditions. Magnetite, Fe_3O_4, is most prevailing in non-oxic conditions and composes of both di- and trivalent iron. The two other oxides, goethite α-FeOOH and especially hematite α-Fe_2O_3, containing only trivalent iron, are prevailing in more oxidizing conditions. These two latter are the most abundant iron oxides in soils.

Experimental

Minerals

The mineral powders used in the batch sorption experiments were Alfa Aesar (Ward Hill, MA, USA) produced goethite (α-phase, Powder), hematite (α-phase, nanopowder, 98 % metals basis, 30-50 nm APS Powder) and magnetite (98 % metals basis, 20-30 nm APS

Powder). Specific surface areas were measured at the Chalmers University of Technology, Sweden, with the Kr-BET method.

Batch sorption experiments

Batch sorption experiments were performed to determine the sorption isotherms for carbonate and to study the effect of pH and ionic strength on the sorption. For sorption isotherms, samples with various concentrations of $NaHCO_3$ and 0.01 M TRIS buffer (tris(hydroxymehthyl)aminomethane) (pH 8.2) were prepared and radiolabeled with 18.5 kBq of $NaH^{14}CO_3$. The minerals were added into these solutions as suspensions in MilliQ water to achieve a sample volume of 20 mL (Milli-Q® system with Quantum® polishing cartridge, Merck, Germany). The solid to liquid ratio was 5 g/L and initial ^{14}C activity concentration 925 Bq/mL. The samples were left to equilibrate under shaking for one week in capped vials. Activity standard for the radioactivity measurement was prepared by adding MilliQ water instead of the mineral-water suspension and background sample by adding stable $NaHCO_3$ without the tracer.

After the equilibration period, aliquots of the samples were ultracentrifuged and 0.5 mL subsamples of the supernatants were mixed with 1 mL of 0.1 M NaOH to prevent degassing of HCO_3^- as CO_2. Finally, 10 mL of OptiFluor LSC cocktail was added to each sample and the samples were measured for ^{14}C with Hidex 300 SL liquid scintillation spectrometer. The TDCR (triple-to-double coincidence ratio) was used as a counting efficiency determination method of each sample.

The fraction of sorbed carbonate ions was calculated from the decrease in the activity concentration of the solution assuming isotopic equilibrium between stable and radioactive carbonate ions.

The Langmuir isotherm equation

$$q = \frac{q_0 K_L c}{1 + K_L c} \qquad (1)$$

where q is the sorbed amount (in mol/kg mineral) and c the carbonate ion concentration in the solution was used to find the constants q_0 and K_L that represent the maximum sorption (mol/kg) and equilibrium constant for the sorption reaction, respectively. A non-linear curve fit to the experimental q over c data using fitting equation (1) was performed using OriginPro 8.6 software. Moreover, the surface site density was calculated from the maximum sorption and specific surface area of the minerals.

In order to study the effect of pH and ionic strength on the sorption, sets of samples were prepared as described above at three different ionic strengths (0, 0.01 and 0.1 M) using NaCl as the background electrolyte and HCl and NaOH for pH adjustment. The $NaHCO_3$ concentration in the samples was kept at $5 \cdot 10^{-5}$ M and the initial ^{14}C activity concentration at 925 Bq/mL. Also these samples were allowed to equilibrate for one week, which after the samples were ultracentrifuged and supernatant activity was measured as described above.

From the activity measurement results, the distribution coefficient K_d was calculated using equation

$$K_d = \frac{A_0 - A}{A} \times \frac{V}{m} \qquad (2)$$

where A_0 and A are the initial and final activity concentrations (Bq) of the solution, respectively, and V and m the sample volume (L) and mass (kg), respectively.

The pH values of the remaining suspensions were measured using a glass electrode. For all the sorption isotherm samples, the pH remained constant at 8.2 ± 0.2. For the pH dependent samples, the samples having a pH value lower than 6.5 were excluded from the results as inorganic radiocarbon may gas out as CO_2 at low pH.

As only very low sorption of carbonate on magnetite was observed in studied conditions it is not discussed in detail in the further treatment.

Zeta potential measurements

The zeta potentials of goethite and hematite were measured using a Malvern Zetasizer instrument. For these measurements 0.5 g/L suspensions of each mineral was prepared in MilliQ water, 0.01 M NaCl or 0.1 M NaCl. pH of the suspensions was adjusted using

0.01 M HCl or NaOH. The solutions were left to equilibrate in capped polyethylene vials for one week before the measurement of zeta potential. Due to what is considered random noise in the zeta potential data, smoothed curves as 5-point moving average were produced using OriginPro 8.6 software in order to find the isoelectric points (IEP) of the minerals.

Geochemical modelling

The sorption of carbonate on goethite and hematite was modelled with PhreeqC Interactive using a generalized double-layer surface complexation model (Dzombak & Morel, 1990) and the phreeqc.dat database. IEP values were obtained from Zeta potential measurements and sorption site densities from Langmuir fitting of the carbonate sorption isotherms. Based on the works of Appello et al. [16], Brechtbühl et al. [14], Villalobos et al. [13] and van Geen et al. [11] on carbonate sorption on hematite and goethite the sorption was considered to consist of two reactions:

$$Fe - OH + CO_3^{2-} + H^+ \leftrightarrow Fe - O - CO_2^- + H_2O \quad (3)$$

$$Fe - OH + CO_3^{2-} + 2H^+ \leftrightarrow Fe - O - CO_2H + H_2O \quad (4)$$

resulting from ligand exchange reactions of carbonate and bicarbonate ions.

In the model, the oxide/water interface is presumed to be composed of two layers of charge: a surface layer and a diffuse layer of counterions in solutions. As a result, all specifically adsorbed ions are assigned to the surface layer, while all non-specifically sorbed counterions are assigned to the diffuse layer [11,17]. The charge of an oxide surface is determined by proton transfer reactions and surface coordination reactions. The dependence of surface charge on pH is attributed to protonation and deprotonation reactions of the surface sites:

$$Fe - OH + H^+ \leftrightarrow Fe - OH_2^+ \quad (5)$$

$$Fe - OH \leftrightarrow Fe - O^- + H^+ \quad (6)$$

Apparent equilibrium constants for these surface species for different minerals can be calculated from zeta potential data as the reactions (5) and (6) are affected by the variable charge of the oxide surface.

Using IEP values and sorption site densities, the surface complexation constants of the reactions (3) and (4) were modelled to best fit with the carbonate isotherm data.

The CO_2 saturation indices for the solutions in sorption isotherm samples were checked with PhreeqC modelling to fall under -3.42 (corresponding to atmospheric CO_2 concentration of 380 ppm). Sorption isotherm data exceeding this SI value was excluded from further calculations because degassing of carbon dioxide from these solutions could not be ruled out.

Results and discussion

Isoelectric points and specific surface areas of the minerals

The zeta potential of hematite and goethite at three ionic strengths as a function of pH are shown in Fig. **1**. The data suffers from irregularities that are considered as noise and the curves show the smoothed data that was used to find the isoelectric point of the minerals. For goethite, the ionic strength had no significant effect on the isoelectric point which was found to fall between pH values 9.1 and 9.3. Here the IEP of goethite is taken as 9.2 ± 0.1. For hematite, the IEP varied between 6.5 and 6.9, and thus the value 6.7 ± 0.2 was selected for the IEP of hematite. The IEP values determined were used in the modelling of the sorption results. The reported IEP values of iron oxides vary considerably from one product to another, in the range 7.4-9.4 for goethite and 7.0-9.3 for hematite [15]. Our value for hematite lies in the upper end of the range while that of goethite falls below the reported range. Based on the observed values one would assume that hematite would be the most efficient in anion sorption due to its positive surface up to pH 9.3 while goethite would hardly take any anions at relevant groundwater pH values between 7 and 9. This will be discussed later. The reported IEP value for magnetite lies in the range 6.0-6.8 being logical with our observation of no carbonate sorption taking place [15]. The measured specific surface area values were 15.8 ± 0.1 g/m^2, 113 ± 0.2 g/m^2 and 41.0 ± 0.1 g/m^2 for goethite, hematite and magnetite, respectively.

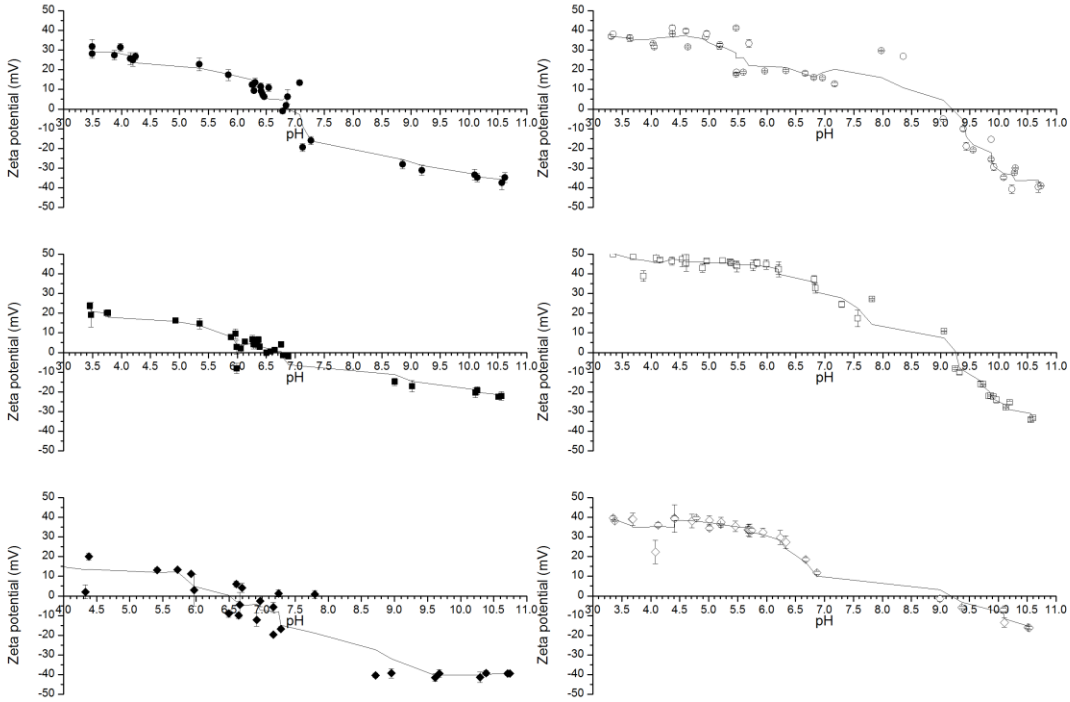


Fig. 1 The zeta potentials of hematite (right-hand side) and goethite (left-hand side) as a function of pH. Hematite in MilliQ water (,), 0.01 M NaCl (!) and 0.1 M NaCl (Λ) and goethite in MilliQ water (–), 0.01 M NaCl (∀) and 0.1 M NaCl (M). The smoothed curves show the 5-point moving average of the data.

Sorption isotherms

The carbonate sorption isotherms for goethite and hematite were rather similar (Fig. 2). The sorption of carbonate on magnetite was at a very low level of about 1 mmol/kg at maximum and thus magnetite is not further discussed. The measured carbonate sorption data of goethite and hematite could be reproduced well with the Langmuir equation as is seen in Figure 2 on the right. The constants q_0 and K_L are given in Table 2 along with the

specific surface areas and calculated sorption site densities. For goethite, the pH 8.2 in the sorption isotherm samples was less than the IEP 9.2 and the surface of the mineral was thus cationic which favors the sorption of carbonate ions by anion exchange or surface complexation. However, for hematite the IEP of 6.7 was lower than that in the batch experiments, which implies an anionic surface for hematite and thus anion exchange is not a feasible sorption mechanism.

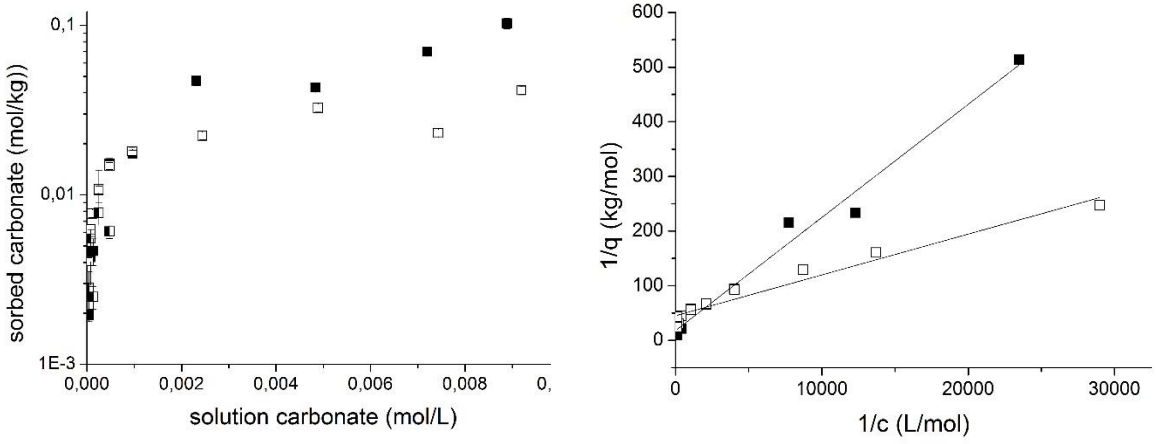


Fig. 2 Sorption isotherms of carbonate ions on hematite (!) and goethite (∀) at pH 8.2 ± 0.2 (left) and Right the Langmuir fittings of the results (right).

Table 2. *The maximum sorption q_0, sorption equilibrium constant K_L, the adjusted R^2 of the non-linear curve fit, the specific surface area s and sorption site density d for the sorption of carbonate ions on hematite and goethite.*

Mineral	q_0 **(mol/kg)**	K_L **(L/mol)**	**Adj. R^2**	**s (m^2/g)**	**d ($1/nm^2$)**
Hematite	0.056	660	0.985	113 ± 0.5	0.30
Goethite	0.022	6010	0.959	15.8 ± 0.1	0.84

Effect of ionic strength and pH

At pH 6.5-7.0 the distribution coefficient of carbonate on hematite and goethite were at the same level, at 100-300 mL/g (Fig. 3). At higher pH values K_d decreased systematically, for hematite more drastically, being below 10 mL/g already at pH 8 while for goethite the K_d remained above this value up to pH 10.5. This behavior is logical considering the IEPs of the minerals, 6.7 for hematite and 9.2 for goethite. The declining trend was as expected because the positive charge of the mineral surfaces decreases as the pH increases and thus the sorption of carbonate decreases. Furthermore, as the pH decreases the speciation of carbon changes from carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-) and finally to carbon dioxide (CO_2) (Fig. 4). This decreases the negative charge of the sorbing species and, consequently, decreases the sorption on negatively charged mineral surfaces. Thus, as the pH decreases there are two factors acting to opposite directions: increasing protonation favors sorption while protonation of the carbonate ions diminishes it.

The ionic strength had only a slight decreasing effect on the distribution coefficient, which is in line with the fact that sorption mechanism is inner-sphere complexation. The decreasing effect caused by the ionic strength can be due to the saturation of sorption sites caused by the interactions of chloride ions on the plane typically occupied by electrolyte outer-sphere complexes. The negative charge of carbonate complex extending onto the diffuse layer is highly influenced by the electrostatic field created by the adsorption of electrolyte anions, such as chloride ions, on this plane [13]. Therefore, an increase in ionic strength causes an increase of negative charge on this plane and thus a decrease in carbonate adsorption. Furthermore, in higher NaCl concentrations sodium complexes play a more significant role in the speciation of carbon and, at higher pH values $NaCO_3^-$ is a dominating species together with CO_3^{2-} (Fig. 4).

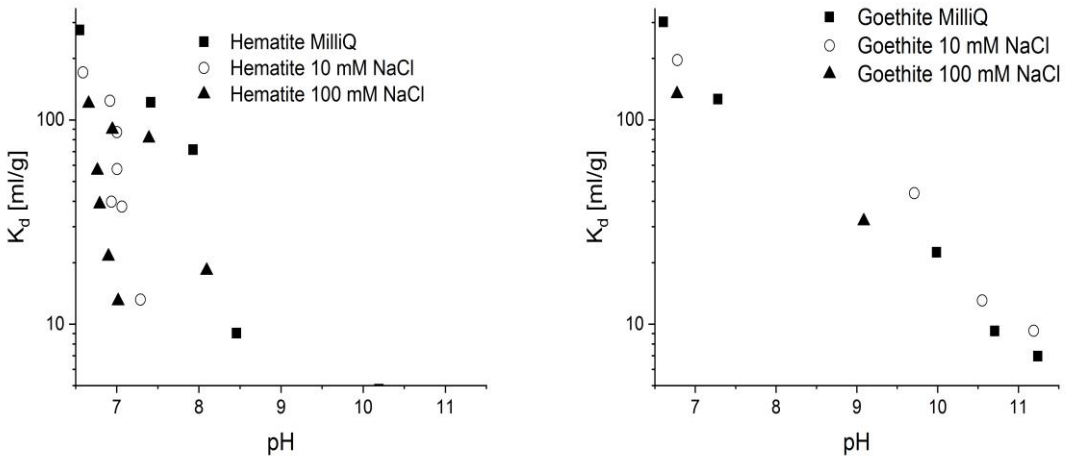


Fig. 3 Distribution coefficients of carbonate on hematite (left) and goethite (right) as a function of pH in MilliQ, 10 mM NaCl and 100 mM NaCl solutions.

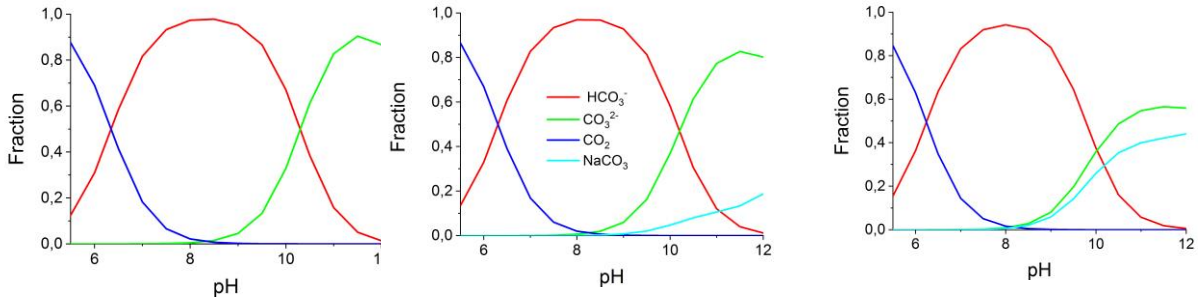


Fig. 4 Aqueous speciation of carbon. Left: MilliQ, Middle: 0.01 mM NaCl, Right: 0.1 mM NaCl modelled with PhreeqC. Thermodynamic data from phreeqc.dat was used.

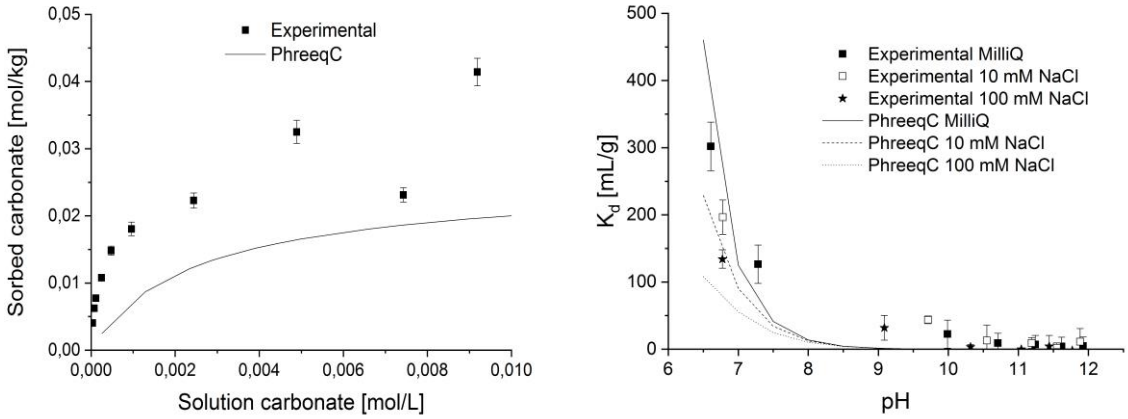
Geochemical modelling

The sorption results were modelled with PhreeqC using a generalized double-layer surface complexation model using IEP values obtained from Zeta potential measurements and the sorption sites densities obtained from specific surface area measurements and the Langmuir isotherms. Surface complexation constants for the two reactions described in Equations 3 and 4 were obtained from the best fit with experimental isotherm data (Table 1). As a starting point in modelling of surface complexation constants the values reported

by Appelo et al. [16] and Brechbühl et al. [14] were used. The model was able to reproduce well the pH dependent sorption results of carbonate on goethite, but underestimated the concentration dependent results (Fig 5). The sorption site density 0.84 sites/nm^2 used in the model was considerably smaller than 2.31 sites/nm^2 used by Van Geen et al. [11] and by Dzombak and Morel [17], which may explain the low modelled sorption compared to experimentally observed one. However, the fitting of the pH dependent results would suffer from increasing the sorption site density. The surface complexation constants obtained from the fitting (12.36 and 20.12) were close to the values (12.78 and 20.37) obtained by Appelo et al. [16] in a similar study.

Table 1. *Surface complexation constants for carbonate sorption on goethite and hematite used in this study.*

Surface complexation constants	**log *K***
Surface acid-base reactions on goethite	
Hfo_wOH = Hfo_wOH	0
Hfo_wOH + H^+ = Hfo_wOH_2^+	6.7
Surface acid-base reactions on hematite	
Hfo_wOH = Hfo_wOH	0
Hfo_wOH + H^+ = Hfo_wOH_2^+	9.2
Carbonate sorption on goethite	
Hfo_wOH + CO_3^{2-} + H^+ = Hfo_wCO_3^- + H_2O	12.36
Hfo_wOH + CO_3^{2-} + 2H^+= Hfo_wHCO_3 + H_2O	20.412
Carbonate sorption on hematite	
Hfo_wOH + CO_3^{2-} + H^+ = Hfo_ wCO_3^- + H_2O	10.92
Hfo_wOH + CO_3^{2-} + 2H^+= Hfo_wHCO_3 + H_2O	22.94

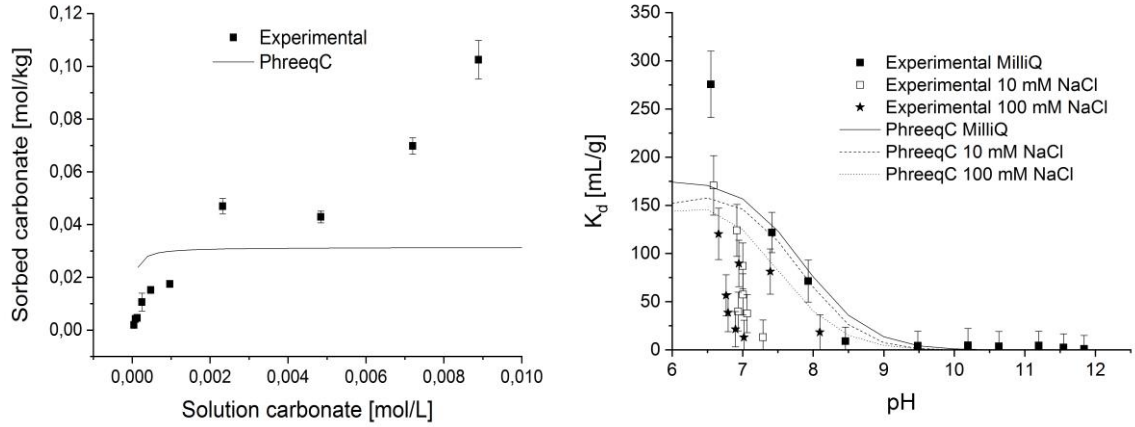


279

280 **Fig. 5** The modelled sorption isotherms of carbonate on goethite.

281

282 The generalized double-layer surface complexation model reproduced the sorption results
283 of carbonate on hematite rather adequately (Fig 6). The surface complexation constants
284 obtained from the fitting (10.92 and 22.94) were the same as the values (10.92 and 21.94)
285 obtained by Brechbühl et al. [14] in a similar study while the sorption site density used in
286 this study 0.30 sites/nm^2 was considerably smaller than 12 sites/nm^2 used by Brechbühl et
287 al. [14].



288

289 **Fig. 6** The modelled sorption isotherms of carbonate on hematite.

290

Conclusions

Carbonate was found to be considerably sorbed on goethite and hematite, but the sorption on magnetite was negligible in all studied conditions. Sorption on goethite and hematite was largest in the neutral pH-range and it decreased with increasing pH. This is caused by the decreasing positive charge of the mineral surface as the pH increases. As pH decreases the speciation of carbon changes from carbonate to bicarbonate and finally to carbon dioxide decreasing the sorption, as the bicarbonate is less preferred compared to carbonate. Carbonate sorption was also observed to slightly decrease with increasing ionic strength, which can be due to the saturation of sorption sites caused by the interactions of chloride ions on the plane typically occupied by electrolyte outer-sphere complexes. The batch sorption results were modelled with the generalized double-layer surface complexation model and the model was able to reproduce rather well the experimental sorption results.

Considering the long-term consequences of the final disposal of spent nuclear fuel, we may conclude that radiocarbon is not completely non-sorbing as presently is assumed in conservative safety analyses. In addition to isotopic exchange reaction of carbonate with calcite the sorption on iron oxides is a retarding process preventing rapid migration of radiocarbon into the biosphere.

Acknowledgements

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